Base-Catalyzed Reactions in NH_3-Enriched Near-Critical Water

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Abstract: Near-critical water (NCW) has drawn increasing attention as an environmentally benign medium for organic chemical reactions, especially acid/base catalysis without added acid or base. However, problems such as slow reaction rate and poor selectivity exist for these organic syntheses in NCW, which greatly hinder the applications of the attractive technique in industrially interesting processes. We developed a novel solvent system to accelerate base-catalyzed reactions by the addition of NH_3 to NCW. The reactions demonstrated include hydrolysis of cinnamaldehyde and aldol condensation of phenylaldehyde with acetaldehyde. The reaction kinetics of the two reactions were determined. The effects of the amounts of added NH_3 and temperature on the reactions were also investigated. The results demonstrate the feasibility of using NH_3-enriched NCW as an environmentally benign reaction medium for the acceleration of base-catalyzed reactions.

Key words: near-critical water, base-catalyzed reactions, NH_3

Introduction

Near-critical water (NCW), as an environmentally benign medium, has drawn increasing attention for organic chemical reactions[1-4]. NCW has a strong tendency to ionize and can act as an acid and/or base catalyst. In addition, NCW can dissolve organics to some extent allowing for a homogenous reaction within an aqueous phase. Extensive research [5-14] has been pursued on acid/base-catalysis reactions without added acid or base in NCW. However, problems such as slow reaction rate and poor selectivity exist for these non-catalyzed organic syntheses in NCW, which greatly hinder the applications of the attractive technique in industrially interesting processes. Savage et al. [15] studied CO_2-enriched NCW to accelerate dehydration of cyclohexanol to form cyclohexene and the alkylation of p-cresol with tertbutyl alcohol to form

2-tert-butyl-4-methylphenol in NCW. Torry et al. [16] explored the effects of salts on hydrolysis of dibenzyl ether and benzyl phenyl amine in supercritical and near-critical water. Here, we proposed a novel solvent system to accelerate base-catalyzed reactions by the addition of NH_3 to NCW, i.e., NH_3-enriched NCW. As ammonia can be easily recycled by heating, NH_3-enriched NCW is considered as an environmentally benign solvent. As demonstrations, the hydrolysis of cinnamaldehyde and aldol condensation of phenylaldehyde with acetaldehyde in NH3-enriched NCW are reported in this paper.

1 Experimental

1.1 Reagents

Cinnamaldehyde, benzaldehyde, acetaldehyde, ethanol, aqueous ammonia, are all A.R. from Hangzhou Chemical Reagent Co. Ltd. Acetaldehyde was re-distilled before use. Others were used as received.

1.2 Apparatus and procedure

Fig. 1 is the schematic diagram of the experimental apparatus, which mainly consists of a high pressure batch reactor (500mL), a buffer vessel (1L), a plunger pump and a sampling line. The sampling line includes three high-pressure valves, a sample loop between V10 and V11 with a volume of 0.3 mL. V10, V11 and the sample loop is fixed on an iron support. The tubing is 1/16″ OD×0.030″ ID (SUS316) before V11 and 1/16″ OD×0.006″ ID (SUS316) after V11.

Experimental procedure: first, the system was degassed with vacuum pump, and then filled with high purity nitrogen. 350 mL of deionized water was added into the reactor by plunger pump, and the system pressure was increased to 10MPa by high pressure nitrogen cylinder. After the temperature inside the reactor reached the reaction temperature, 30 mL of reactants (for hydrolysis, cinnamaldehyde-ethanol solution; for aldol condensation, benzaldehyde-redistilled acetaldehyde mixture) were quickly injected and the line was rinsed with 20ml ethanol. The reactor reached the reaction temperature within several minutes. The system pressure was maintained at 15MPa. Finally, collected samples at the certain reaction time. The reaction content was constantly agitated at 600 rpm using a mechanical impeller throughout the reaction.

Sampling procedure: Samples were collected after 1-2 mL solution was vented to rinse the sample line. Then closed valves and took off the sampling loop together with V10 and V11.

Finally, discharge the samples into a volumetric flask, wash the sampling loop with anhydrous ethanol and fill the volumetric flask with anhydrous ethanol. The pressure drop (0.1~0.2 MPa) during sampling was compensated by injecting water into the buffer vessel.

The apparatus has the following features:

- Temperature up to 350℃, pressure 30MPa.
- Good temperature control ±1℃.
- On-line sampling.
- Small pressure variation because of the buffer vessel installed.
- Resistance to corrosion. The reactor is made of Titanium Alloy TC4.

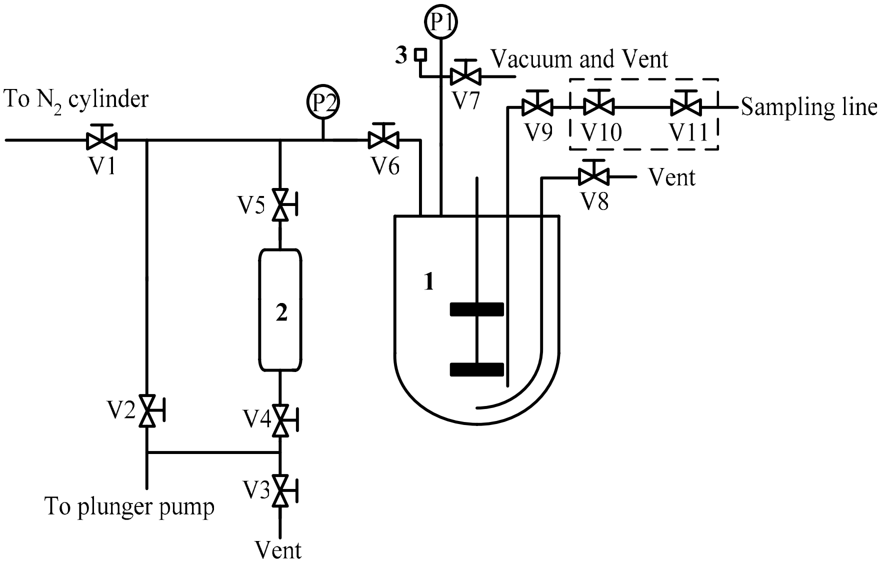


Fig. 1 The schematic diagram of the experimental apparatus

1. high-pressure reactor 2. buffer vessel 3. safety valve V1~V11 high-pressure valve P1、P2 pressure gauge

1.3 Analysis

The liquid sample was quantitatively analyzed by GC (Agilent 1790F) with FID detector and dodecanol as an internal standard. GC column was FFAP (30m×0.32mm i.d.×0.4μm). Column temperature, detector temperature, injector port temperature were set at 200℃, 250℃, 220℃, respectively. Injection volume was 1μL. Typical GC chromatograph of the product was shown in Fig. 2. Peak identification was made by comparison of sample peak retention times with the standard solutions of pure compounds, and conformed with GC/MS (Agilent 6890GC/5973MSD).

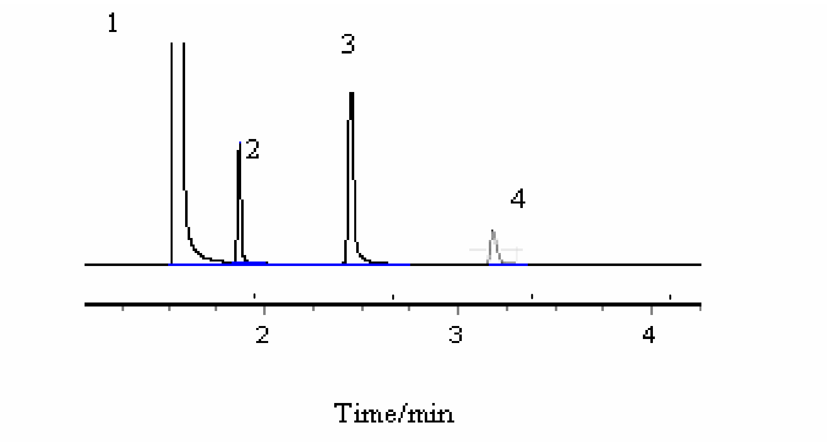


Fig. 2 Typical GC chromatograph of the product: 1—ethanol(1.524 min); 2--benzaldehyde (1.884 min); 3—dodecanol(2.456 min); 4—cinnamaldehyde(3.244 min)

2 Results and discussion

2.1 Hydrolysis kinetics of cinnamaldehyde in NH_3-enriched NCW

2.1.1 Effect of the amounts of ammonia

The effects of the amount of ammonia added and residence time on the cinnamaldehyde conversion and benzaldehyde yield are shown in Fig. 3 and Fig. 4, respectively. The reactions were carried out at 240℃ and pressure of 15MPa. The results show that with the increasing amount of ammonia, both the reaction rate of the cinnamaldehyde hydrolysis and the yield of benzaldehyde are greatly enhanced.

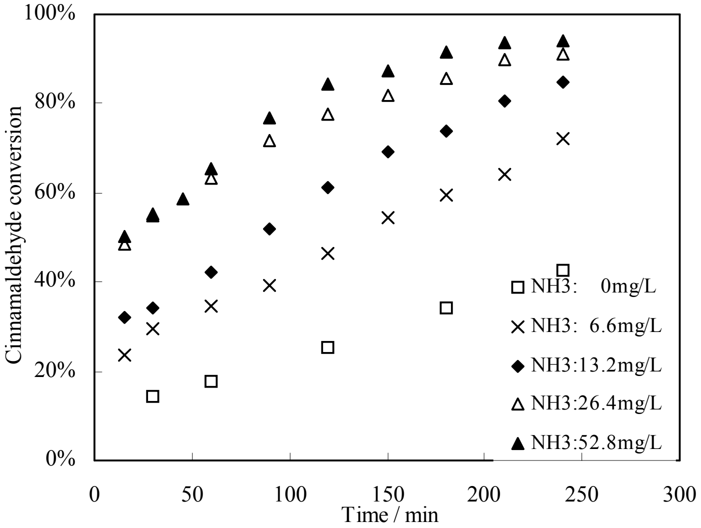


Fig. 3 The effects of the amount of ammonia added and residence time on cinnamaldehyde conversion

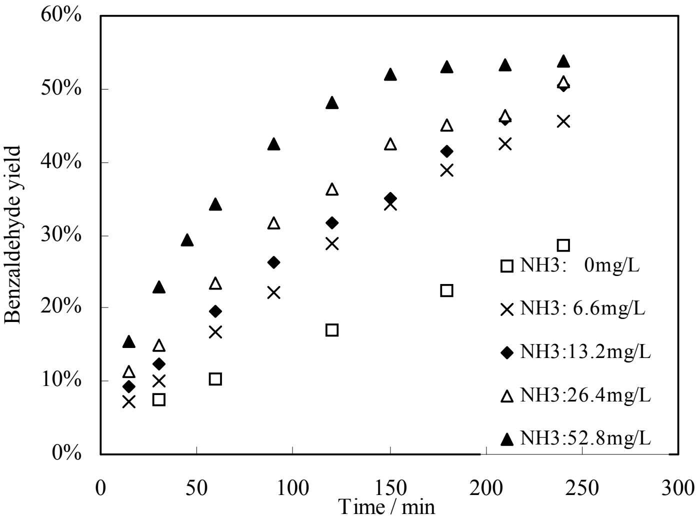


Fig. 4 The effects of the amount of ammonia added and residence time on benzaldehyde yield

2.1.2 Effect of reaction temperature

The effects of reaction temperature and residence time on cinnamaldehyde conversion and benzaldehyde yield are depited in Fig. 5 and Fig. 6 with the addition of NH_3 at 13.2 mg/L, pressure at 15MPa. Reaction temperature appears to have significant influence on the cinnamaldehyde conversion and benzaldehyde yield. As the reaction temperature increases, cinnamaldehyde conversion increases and a maximum yield of benzaldehyde can be seen at temperature ≥280℃, indicating the unstability of benzaldehyde in NCW at higher temperature.

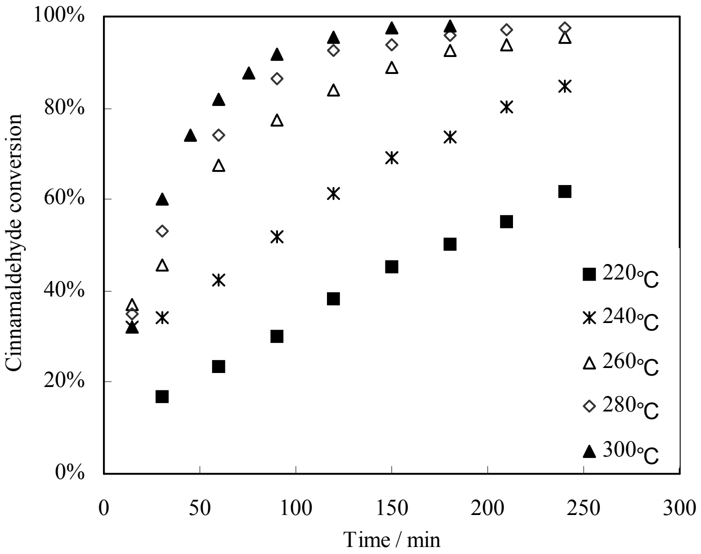


Fig. 5 Effects of reaction temperature and residence time on cinnamaldehyde conversion (NH_3 at 13.2 mg/L)

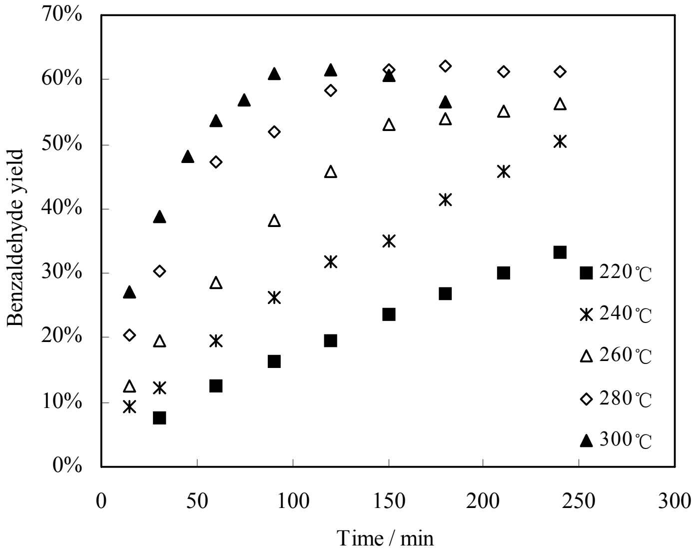
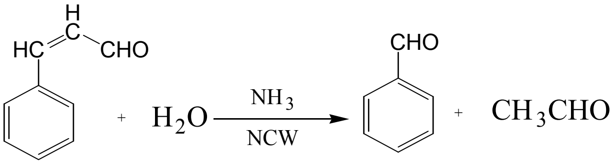


Fig. 6 Effects of reaction temperature and residence time on benzaldehyde yield (NH_3 at 13.2 mg/L)

2.1.3 Kinetics modeling

The reaction scheme is as follows.



Base on the first-order reaction assumption, the equation $\ln C_{A0} - \ln C_A = kt$ was used to correlate the data. The evaluation of rate constants at different temperatures is shown in Fig. 7. Arrhenius plot for cinnamaldehyde hydrolysis is shown in Fig. 8. The evaluated apparent activation energy of cinnamaldehyde hydrolysis is 58.6 kJ/mol.

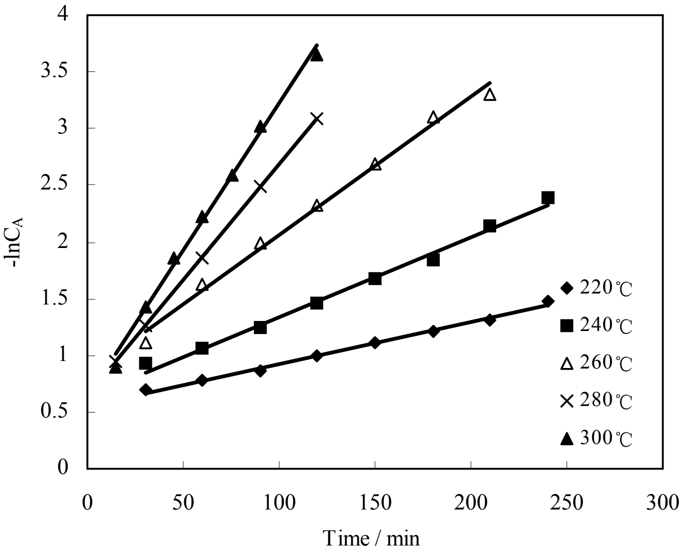


Fig. 7 Evaluation of rate constants at different temperatures (NH$_3$ at 13.2mg/L)

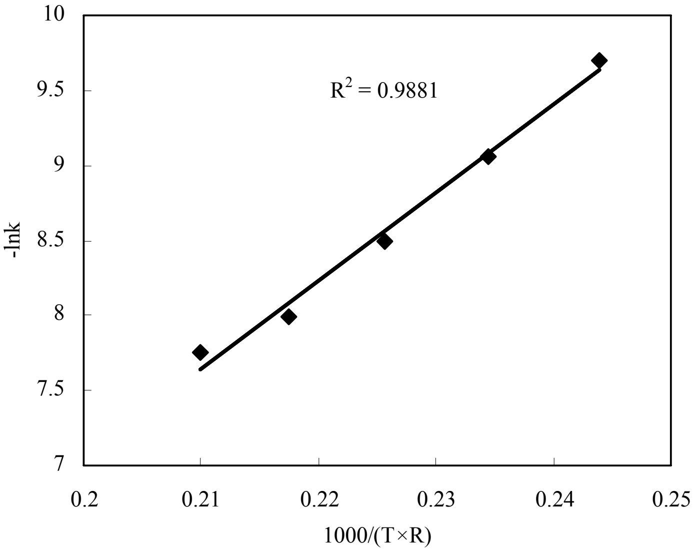


Fig. 8 Arrhenius plot for cinnamaldehyde hydrolysis (NH$_3$ at 13.2mg/L)

2.2 Aldol condensation kinetics of phenylaldehyde with acetaldehyde in NH$_3$-enriched NCW

2.2.1 Effects of the amounts of ammonia

Fig. 9 and Fig. 10 depict the effects of the amount of ammonia added and the residence time on benzaldehyde conversion and cinnamaldehyde yield. The reaction was carried out at 260℃ and at pressure of 15MPa. The molar ratio of benzaldehyde to acetaldehyde was 1:5.7. The results show that the reaction rate of aldol condensation of benzaldehyde with acetaldehyde increases significantly with increasing amount of ammonia added.

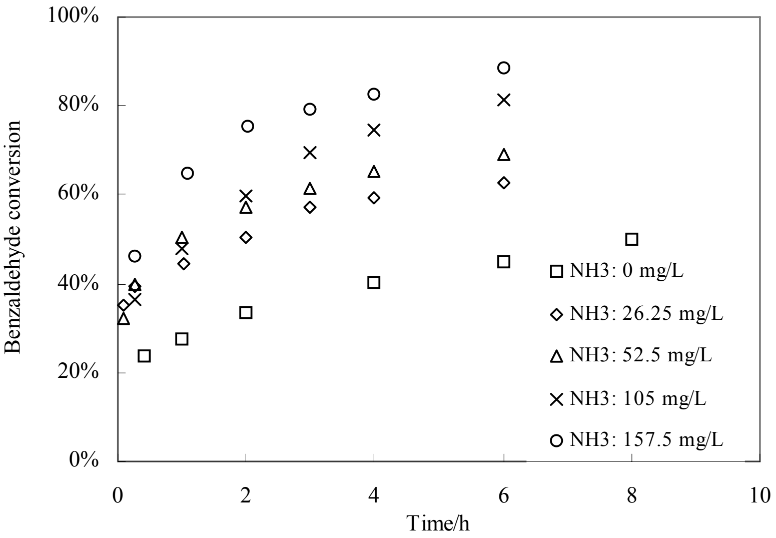


Fig. 9 Effects of the amount of ammonia added and residence time on benzaldehyde conversion

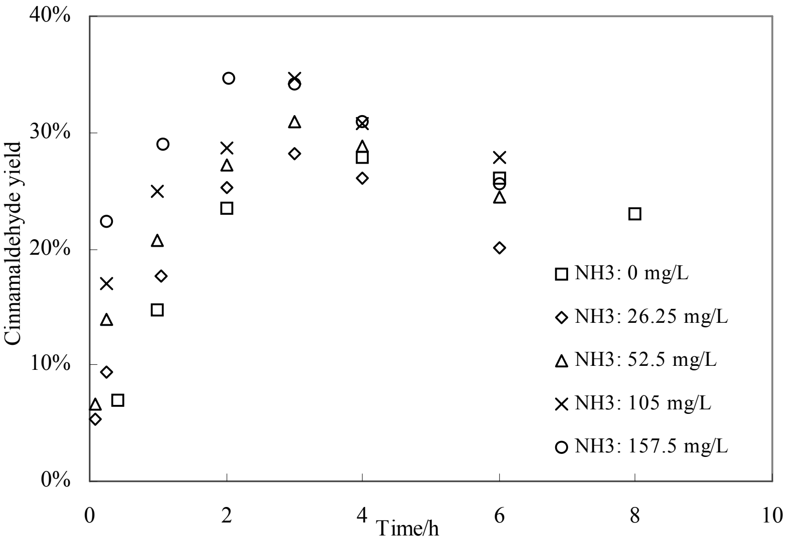


Fig. 10 Effects of the amount of ammonia added and residence time on cinnamaldehyde yield

2.2.2 Effects of reaction temperature

The effects of reaction temperature and residence time on benzaldehyde conversion and cinnamaldehyde yield are shown in Fig. 11 and Fig. 12 with the amount of NH_3 added at 105 mg/L, pressure at 15MPa, the molar ratio of benzaldehyde to acetaldehyde at 1:5.7. Reaction temperature had a great influence on the benzaldehyde conversion. With the increase in reaction temperature, benzaldehyde conversion increases with a maximum cinnamaldehyde yield in the temperature range of 260-280°.

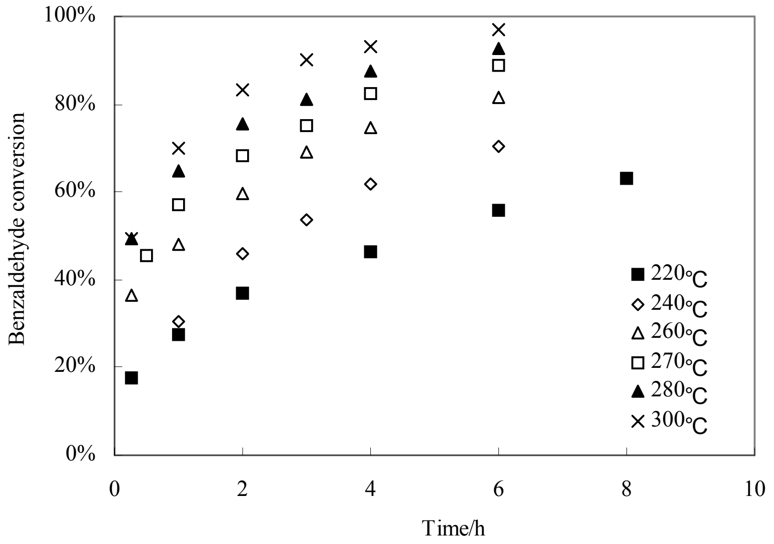


Fig. 11 Effects of reaction temperature and residence time on benzaldehyde conversion (NH_3 at 105 mg/L)

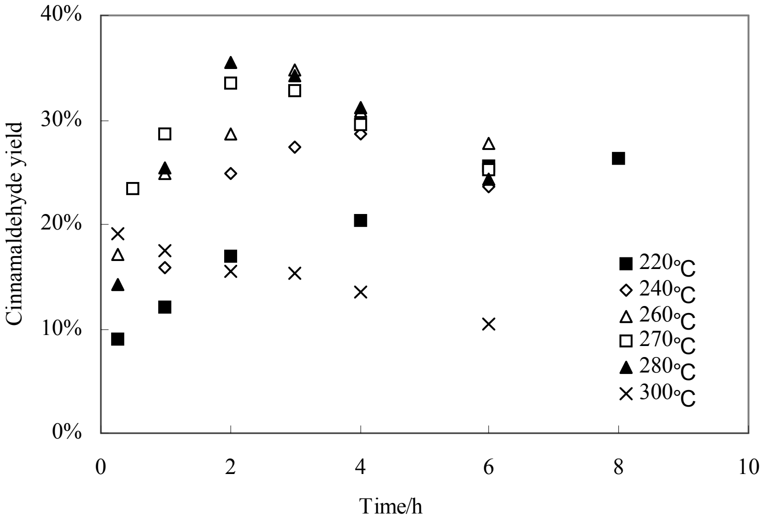
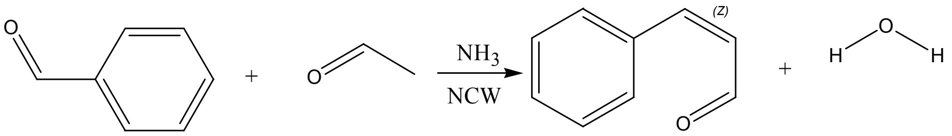


Fig. 12 Effects of reaction temperature and residence time on cinnamaldehyde yield (NH_3 at 105 mg/L)

2.2.3. Kinetics modeling

The reaction scheme is as follows.



Base on the first-order reaction assumption, the equation $\ln C_{A0} - \ln C_A = kt$ was used to correlate the data. Evaluation of rate constants at different temperatures was shown in Fig. 13 and Arrhenius plot for aldol condensation was shown in Fig. 14. The evaluated apparent activation energy of aldol condensation of benzaldehyde with acetaldehyde was 42.4 kJ/mol.

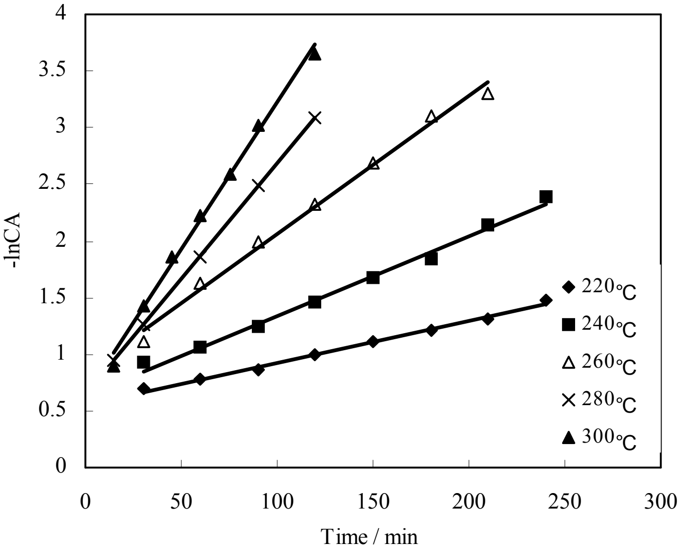


Fig. 13 Evaluation of rate constants at different temperatures (NH_3 at 105 mg/L)

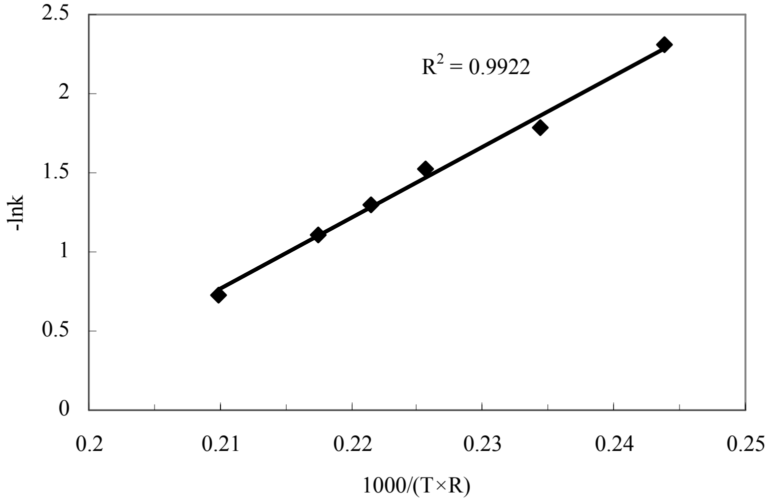


Fig. 14 Arrhenius plot for condensation of benzaldehyde with acetaldehyde (NH_3 at 105 mg/L)

3 Conclusion

As a novel and environmentally benign solvent system, NH_3-enriched NCW was proposed to enhance the reaction rate and improve the selectivity of base-catalyzed organic reactions in NCW. The experimental studies of the hydrolysis of cinnamaldehyde and aldol condensation of phenylaldehyde with acetaldehyde suggest that NH_3-enriched NCW can greatly accelerate the base-catalyzed organic reactions.

Acknowledgements

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